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To study the distribution of radium, we used one or two drops of a titrated solution of a radium salt, added to the original solution of LaF_3 in 3 percent HNO_3 . To prepare the titrated radium salt solution, we used a high-percent radium preparation in which the admixture of barium did not exceed 25 percent.

Since radium has no more stable isotopes, we employed an admixture to the radium consisting of continuously increasing quantities of its closest chemical analogue, barium, which is always truly isomorphous with it, so as to study the variation of concentration of the distributed substance within wide limits. Already in 1940, in the investigation of the reverse system of methylene blue + $\text{Ra}(\text{NO}_3)_2$, we showed that it was admissible and possible to make such a replacement of radium with barium for our purposes (3).

As usual, we first investigated the rate with which equilibrium was attained in the LaF_3 - RaF_2 system. The results are presented in Table 1.

The results from Table 1 show that equilibrium between LaF_3 and the solution in relation to radium is established for practical purposes after 48 hr, while after 8 hr of recrystallization the value $K_d(D)$ can already be calculated as the average of the distribution data given in the second and third columns of Table 1.

For performing all further experiments, data of Table 1 permitted us to choose the time of recrystallization which would guarantee the attainment of equilibrium. None the less, we checked experimentally to see how well the values of $K_d(D)$, obtained for the time we chose, would correspond with each other if we approached them from two opposite sides. As an example, we cite certain data (cf. Tables 2 and 3).

The results of Tables 2 and 3 show conclusively that the time of recrystallization which we chose (60 hr) completely guarantees that equilibrium will be attained with respect to radium between the solid crystalline phase and the solution and that the average values for $K_d(D)$, obtained by reaching the equilibrium from two opposite sides, will coincide within the limits of experimental error.

To explain whether or not the distribution of radium between the crystals and solution of LaF_3 takes place strictly according to the law for the distribution of a substance between two immiscible solvents, we studied within wide limits the effect on the distribution constant $K_d(D)$ of the variation of the concentration of the distributed substance. The results are shown in Table 4. These results show graphically that the value for the distribution constant $K_d(D)$ of radium depends on the concentration of the distributed substance and decreases rapidly as the latter concentration is decreased. In this case, the value of $K_d(D)$ clearly tends toward zero.

Thus, we now have the right to assert that Type III isomorphism, like isomorphism of Type II, is distinguished from Type I, according to the classification of V. Goldschmidt, principally by the fact that when substances which are mutually isomorphous, according to types III and II, form mixed crystals, a lower limit of miscibility is observed which is never observed for isomorphism of Type I. Consequently, when these mixed crystals are formed, whole elementary nuclei of the crystal lattice are replaced, as distinguished from replacement of ion for ion, atom for atom, or molecule for molecule which occurs in the case of Type I isomorphism.

BIBLIOGRAPHY

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3. V. G. Khlopin and M. A. Tolstaya, Zhur Fiz Khim, Vol XIV, p 941 (1940)

[Tables follow.]

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Table 1. Attainment of Equilibrium for Distribution of Ra Between Crystals of LaF_3 and Its Saturated Solution in 3% HNO_3 When Temp = 100°C

Time of Recrystallization (hr)	$K_f(D)$ Active Solution + Inactive Suspension	$K_f(D)$ Inactive Solution + Active Suspension
1	4.6	51.0
4	7.8	41.3
8	10.0	30.4
24	15.6	22.7
48	17.4	19.4
72	18.4	18.0
120	18.2	18.6

Table 2. Distribution of Ra Between an Active Saturated Solution of LaF_3 in 3% HNO_3 and Inactive Crystals of LaF_3 When Temp = 100°C
(total content of Ra + Ba: 3 mg in 30 ml solution)

% La in Solid Phase	% Ra in Solid Phase	Coefficient		
		Enrichment y/x	Impoverishment $(100-y)/(100-x)$	Distribution $K_f(D)$
9.31	65.24	7.01	0.38	18.2
18.37	79.96	4.35	0.25	17.4
27.56	86.30	3.13	0.19	16.5
27.56	87.80	3.18	0.17	18.7
32.13	89.96	2.80	0.15	18.7
Average				18.1

Table 3. Distribution of Ra Between an Inactive Saturated Solution of LaF_3 in 3% HNO_3 and Active Crystals of LaF_3 When Temp = 100°C
(total content of Ra + Ba: 30 mg in 30 ml solution)

% La in Solid Phase	% Ra in Solid Phase	Coefficient		
		Enrichment y/x	Impoverishment $(100-y)/(100-x)$	Distribution $K_f(D)$
7.80	60.0	7.7	0.43	17.8
15.63	78.19	5.0	0.26	19.2
23.15	83.96	3.63	0.20	18.1
35.00	91.02	2.60	0.14	18.6
Average				18.4

Table 4. Dependence of Average Distribution Coefficient $K_f(D)$ Between Crystals of LaF_3 and Its Solutions in 3% HNO_3 for Radium on Total Concentration of Ions of Ra^{++} + Ba^{++} in the Solution When Temp = 100°C

	Total Concentration	
<u>Of Ions Ra... + Ba...</u>	<u>Of Molecules RaF₃ + BaF₃ in mM</u>	<u>Value of K_f(D)</u>
7 · 10 ⁻¹	5.6 · 10 ⁻¹	18.2
2.3 · 10 ⁻¹	1.9 · 10 ⁻¹	13.1
2.3 · 10 ⁻²	1.9 · 10 ⁻²	5.2
2.3 · 10 ⁻⁴	1.9 · 10 ⁻⁴	1.01
2.3 · 10 ⁻⁶	1.9 · 10 ⁻⁶	0.25
< 1.6 · 10 ⁻⁸	< 9.9 · 10 ⁻⁹	0.07

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